EFFECT OF PRESSURE ON THE DIELECTRIC CONSTANT, POWER FACTOR, AND CONDUCTIVITY OF RUBBER-SULPHUR COMPOUNDS

BY

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EFFECT OF PRESSURE ON THE DIELECTRIC CONSTANT, POWER FACTOR, AND CONDUCTIVITY OF RUBBER-SULPHUR COMPOUNDS [1]

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ABSTRACT

The dielectric constant, power factor, and conductivity of rubber-sulphur compounds containing from 0 to 32 percent of sulphur were measured while subjected to pressures ranging from 1 to 700 bars (approximately 690 atmospheres). The dielectric constant and power factor were measured at 1,000 cycles per second and the conductivity at the end of 1-minute electrification. The effect of pressure on each of the electrical properties was found to change with sulphur content. The dielectric constant of specimens containing up to about 7.5 percent of sulphur increased slightly with pressure. For higher percentages of sulphur it decreased with pressure. The power factor of specimens containing up to about 2 percent of sulphur was independent of the pressure. For percentages of sulphur from 2 to about 12 percent, the power factor increased with pressure; for higher percentages of sulphur it decreased with pressure. The conductivity of specimens containing between about 12 and 19 percent of sulphur increased with pressure, while it decreased with pressure for other percentages of sulphur. Curves are presented which show the effect of pressure on these electrical properties for rubber-sulphur compounds of any possible composition.

The effect of pressure on the electrical properties of two specimens of gutta-percha over the same pressure range was determined and the results are given for comparison.

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[1] This paper includes the subject matter used in a dissertation submitted to the board of university studies of The Johns Hopkins University in partial fulfillment of the requirements for a degree of doctor of philosophy. A copy of this dissertation is on file at the library of the university.

I. INTRODUCTION

This paper reports the results of a study on the effect of pressure on the dielectric constant, power factor, and conductivity of rubber-sulphur compounds, and is the third paper of a series dealing with the electrical properties of rubber-sulphur compounds.[2] The previous papers dealt with the effect of sulphur content, temperature, and current frequency on these electrical properties. The results reported in the present paper have been corrected for changes in the dimensions of specimens caused by changes in pressure. The required data for making these corrections were obtained from a detailed study of the compressibility of rubber-sulphur compounds which has recently been completed.[3]

II. METHOD OF DETERMINING ELECTRICAL PROPERTIES

The specimens were made in the form of insulation on wires in order that they might be put in a pressure apparatus consisting of heavy pipes. Each material under test was formed into an insulating cylinder around the wire. The specimen was placed in the pressure apparatus in such a way that the wire core was used as one electrode and the pressure medium as the other. This made a cylindrical capacitor having the material under test as the dielectric. The capacitance, power factor, and conductance of this capacitor were measured when the various pressures were applied.

The dielectric constant, K, of a material is given by the equation

$$K=AC \tag{1}$$

where C is the capacitance of the capacitor having this material as the dielectric, and A is the shape factor of the capacitor. For certain shapes of the capacitor, A may be readily computed from easily determined dimensions and the dielectric constant obtained from a measurement of the capacitance. However, the specimens used in this investigation were not sufficiently uniform and symmetrical to permit the computation of A. Therefore, an indirect method was used in the determination of A. The dielectric constant of the material was determined by means of flat specimens at atmospheric pressure and 25° C as described by Curtis, McPherson, and Scott.[4] The flat specimen for this purpose usually was made at the same time and from the same batch of material as the cylindrical specimen. The value of A for the cylindrical specimen could then be computed from the capacitance measured in the pressure apparatus at atmospheric pressure and 25° C and from the value of K obtained from the flat specimen.

The conductivity, γ, of a material is given by the equation

$$\gamma=BG \tag{2}$$

where G is the conductance of the specimen and B is the shape factor for conductivity. When the electric field is entirely within the

[2] BS Sci. Pap. 22, 398 (1927) S560; BS J. Research 11, 173 (1933) RP585.
[3] BS J. Research 14, 99 (1935) RP760.
[4] BS Sci. Pap. 22, 398 (1927) S560.

dielectric, the shape factor for conductivity is connected with the shape factor for dielectric constant by the equation

$$B=\frac{10^{21}A}{4\pi v^2}=\frac{A}{11.31} \tag{3}$$

where A is the shape factor for dielectric constant when the capacitance is measured in micromicrofarads, and v is the velocity of light in centimeters per second.[5]

The shape factors were corrected for changes in the dimensions of the specimens due to the compressibility of the materials. The compressibility of the copper or aluminum, of which the core was made, was so small that the effect of the change in the dimensions of the core was negligible. Correction was thus made only for the change in dimensions of the rubber, using the values of compressibility given in a former paper.[6]

III. PREPARATION OF SPECIMENS

Each of the carefully mixed rubber-sulphur compounds was formed in a seamless sheath about a wire. Some of the specimens were vulcanized in steam, while the rest were vulcanized in an inert gas. Those vulcanized in steam were dried before measuring.

1. MATERIALS INVESTIGATED

The rubber specimens investigated were vulcanized compounds of rubber and sulphur ranging in composition from 0 to 32 percent of sulphur. The percentages of sulphur were so chosen that the difference in sulphur content between successive specimens was in no case greater than 6 percent and in most cases it was 2 percent or less. Three varieties of rubber were used, "up-river fine Para", "smoked sheet", and purified rubber. The purified rubber was obtained by the process described by McPherson.[7]

The gutta-percha specimens were cut from a cable which had been obtained from a cable manufacturing company in England. This cable had been stored in water since its manufacture about 18 months before.

2. COMPOUNDING OF RUBBER

The rubber was usually mixed with the sulphur on a roll mill in air. In a few cases the mixing was done in an internal mixer in an atmosphere of carbon dioxide. The rubber and sulphur were weighed separately and the batch was weighed after mixing. The weight of the batch seldom differed from the sum of the weights of the constituents by more than 1 part in 1,000. Any greater difference was due to a loss of sulphur during the mixing and the requisite quantity of sulphur was added to correct for this loss.

[5] Since the ratio of the shape factors is the same regardless of the shape of the specimen, this ratio may be derived for the simplest case, i. e., a parallel plate capacitor. For this, neglecting edge effects, $K=C\times\frac{4\pi v^2 d}{10^{21}S}=AC$, and $\gamma=G\times\frac{d}{S}=BG$, where K is the dielectric constant, C is the capacitance in micromicrofarads, d is the thickness, S is the area of the electrode, v is the velocity of light, γ is the conductivity, and G is the conductance. Thus, $\frac{A}{B}=\frac{4\pi v^2}{10^{21}}=\frac{4\pi\times 9\times 10^{20}}{10^{21}}=11.31$.

[6] J. Research NBS 14, 99 (1935) RP760.

[7] BS J. Research 8, 751 (1932) RP449.

3. FORMATION OF SPECIMENS

Each specimen was formed by applying the rubber-sulphur compound concentrically about a wire by means of a commercial extrusion machine which had been adapted for this particular work. Since the various rubber-sulphur compounds could be applied smoothly to the wire in very narrow temperature ranges, it was necessary to control the temperature closely. For this purpose thermometers were placed at strategic points on the machine and an electric heater was added at the point where the insulated wire emerged, since it was not adequately heated by the original equipment. It was necessary to control the temperature by hand, but this could be readily done after a little experience.

4. VULCANIZATION OF SPECIMENS

Most of the specimens were packed in powdered talc and vulcanized in an atmosphere of steam while the others were vulcanized suspended in an atmosphere of dry hydrogen or CO_2 gas. The method of vulcanizing in steam was replaced by a method of vulcanizing in a dry gas when it was observed that some of the sulphur migrated from the rubber to the talc during vulcanization. Subsequent experiments showed that this migration was particularly significant when small samples of high sulphur content were vulcanized in contact with a considerable quantity of fresh talc.

Those specimens vulcanized in steam were coiled in a pan of powdered talc. This pan and its contents were then placed in a steam vulcanizer which had an automatic control on the steam pressure. The steam in the vulcanizer was maintained at the pressure corresponding to the desired vulcanizing temperature.

Those specimens which were vulcanized in an inert gas were placed in a 2-inch pipe, 6 meters in length, which was mounted vertically and which was provided with a steam jacket welded around it. The specimen was fastened at the top and suspended down the length of the pipe. A weight was fastened to the lower end of the specimen to keep it from touching the sides. The gas pressure around the specimen was kept slightly higher than the steam pressure at the vulcanizing temperature. If the pressure on the specimen were not kept above the pressure of the steam at the vulcanization temperature, the specimen became porous. This porosity was probably due to vaporization of the small amount of moisture present in the compound.

The specimens were vulcanized at 150° C for 4 to 15 hours. These relatively long times of vulcanization were used to assure the combination of practically all the sulphur.

5. DRYING OF SPECIMENS

The specimens which were vulcanized in steam were carefully dried before electrical measurements were made on them. Two methods of drying were used. Some of the specimens were placed in a sealed tank in which a vessel of concentrated sulphuric acid had been placed. This tank was kept at the temperature of 25° C while the air in it was kept stirred by a small fan. The specimens were kept in this tank

for 2 or 3 weeks. Other specimens were placed in a vacuum desiccator in which a drying agent had been placed. The desiccator was evacuated and the specimens left in this condition for 1 or 1½ weeks. All the specimens were stored in a dry atmosphere until measurements were made.

IV. APPLICATION OF PRESSURE TO SPECIMENS

The specimens, each of which was about 6 meters in length, were put in the pressure apparatus in such a way that one end was fastened to a special plug through which electrical contact was brought to the outside of the apparatus. An insulating compound was placed over the ends of the specimen to insulate the wire core from the pressure medium. The wire was used as one electrode in the electrical measurements while the pressure medium was used as the other.

1. APPARATUS FOR APPLYING PRESSURE TO SPECIMENS

A schematic drawing of the apparatus used for applying hydrostatic pressure to the specimens is shown in figure 1. It consisted of 3 parallel steel pipes 6 meters long of the grade known commercially as "double extra heavy." These pipes were connected together and to the pump and pressure gage by means of the proper fittings. The free end of each pipe was about 13 cm lower than the other end, which allowed the air to be removed from the system at the plug opening at the top of the apparatus.

This apparatus was designed so that either water or mercury could be used as the pressure medium around the specimen. The lowest pipe was provided for use with mercury. It was made the lowest part of the apparatus so that mercury could be placed in it around the specimen and yet the pressure could be transmitted from the pump to the surface of the mercury by water. The mercury was introduced through the opening in the top of the apparatus by means of a long-stemmed funnel. An electrical-contact system was used to determine when the proper level had been reached.

To facilitate the making of tight joints lead rings were used in the fittings wherever possible. The lead was forced firmly against the threads of the pipe by the set screws. Lead rings, however, could not be used in the part of the apparatus where mercury was used because of the action between mercury and lead. In this case the joints were made tight by heating the parts, applying "universal" wax and screwing them together while still hot. It was found possible to make the joints so tight that when a pressure of 700 bars [8] was applied to the system and the valve closed, the pressure would not decrease by more than 30 bars in 24 hours.

2. MOUNTING OF SPECIMENS

The specimens were mounted as shown in figure 1. The specimen extended down the length of the pipe and was connected at one end to the special plug. This plug, through which electrical contact was made to the core of the specimen, was so designed that the insulated terminal would not creep under the pressure used. A hard-rubber bushing, which was flared at the inner end, was screwed into a hole

[8] A bar is defined as 10^6 dynes per square centimeter and is equal to 0.987 normal atmosphere.

through the center of the steel plug. The bushing extended about 2½ cm beyond the outer end of the steel plug. The insulated terminal consisted of a brass rod which was flared on the inner end. This was screwed into a hole in the hard-rubber bushing. This terminal extended about 2½ cm beyond the bushing. A small threaded hole was placed in the flared end of the brass terminal and the wire core of the specimen was screwed into this.

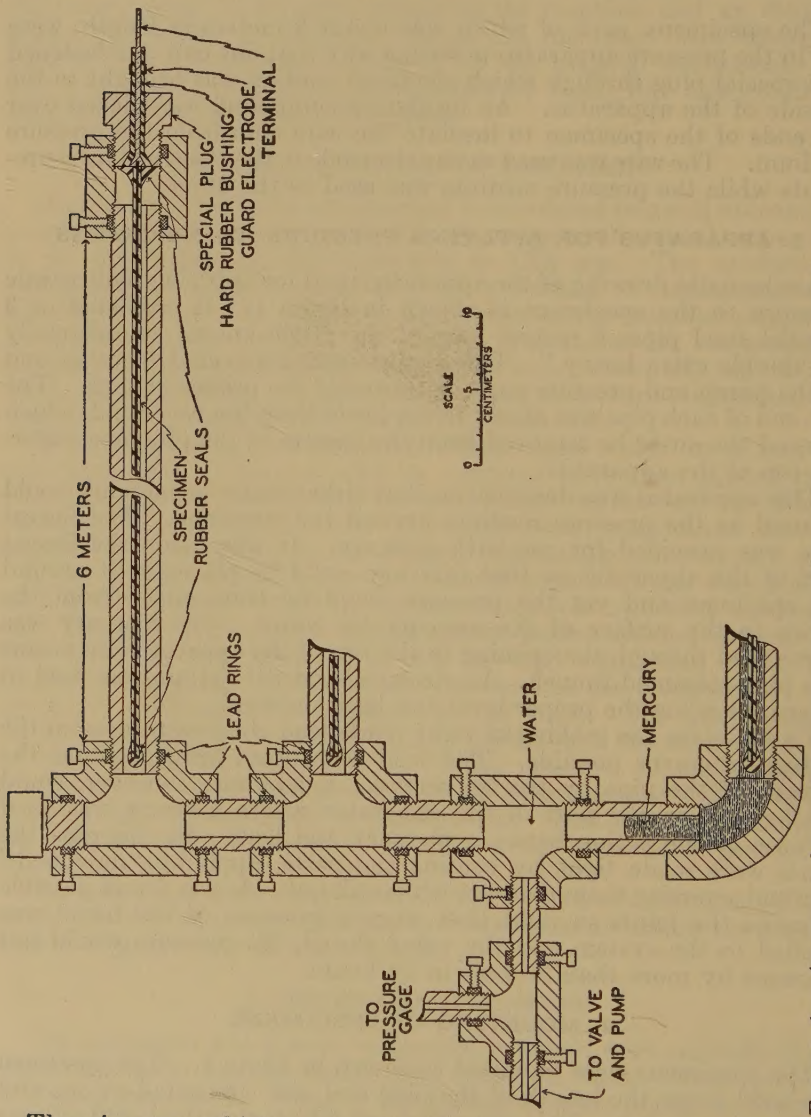

FIGURE 1.—*Apparatus for applying pressure to rubber specimens while electrical measurements are being made on them.*

The wire core, which was used as the inner electrode, was effectively insulated from the pressure medium at both ends by covering them with a thermoplastic insulating (DeKhotinsky) cement or a vulcanized-rubber mixture. The thermoplastic cement was used in the earlier measurements. Rubber was used later because it was found to be more reliable and durable.

The thermoplastic cement was applied by preheating the parts and working the softened material into place. When this material was used the coupling as well as the plug was removed from the pipe. The core of the specimen was attached to the inner end of the terminal in the plug. The coupling and plug were then heated to about 150° C and melted cement was poured over the face of the plug and around the specimen to a depth of about 2 cm. The cement was applied to the loose end of the specimen by heating it and working a ball of warm cement over it.

The rubber compound which was used to insulate the ends of the specimen core from the pressure medium was a soft, easily worked compound designed for rapid vulcanization. When this was used only the special plug was removed from the pipe. The end of this plug was coated with a thermoprene cement known commercially as Vulcalock Cement. After the core of the specimen had been attached to the terminal of the plug the soft unvulcanized-rubber compound was worked around the specimen and over the end of the plug, as shown in figure 1, with the aid of a little heat. A small ball of the rubber was also worked over the loose end of the specimen. The loose end and the plug were placed in an oven in such a way that only a few centimeters of the specimen were exposed to the heat of the oven. The oven was kept at a temperature of about 125° C until the compound was vulcanized.

V. ELECTRICAL MEASUREMENTS

The electrical measurements made on the specimens under pressure were the capacitance, power factor, and conductance.

1. CAPACITANCE AND POWER FACTOR

The capacitance and power factor were measured at 1,000 cycles per second by means of the modified Rosa bridge described by Scott, McPherson, and Curtis.[9] The capacitance between the wire core and the pressure medium surrounding the specimen was measured by a substitution method. Connections were made to the pipes and to the insulated terminal of the plug. This measurement included the capacitance in the plug, which was found to be of the order of 3 micromicrofarads. This excess capacitance was probably approximately counterbalanced by the decrease in capacitance of the specimen due to the sealing compound covering short lengths of the specimen at each end. About 1 cm was covered at the loose end, while about 1.5 cm was covered at the other end. While the exact error in capacitance due to the sealing compounds could not be determined, it was opposite in sign to the error due to neglecting the capacitance in the plug and it was assumed that the resulting error was negligible in comparison to the capacitance of the specimen which was usually about 2,000 micromicrofarads.

2. CONDUCTANCE

The conductance was measured by means of the direct deflection method described by Scott, McPherson, and Curtis.[10] A potential of 300 volts was used for this measurement. The readings were taken at the end of 1 minute after the potential was applied. Each

[9] BS J. Research **11**, 173 (1933) RP585.
[10] See footnote 9.

specimen was short-circuited for 2 minutes before a measurement was made in order to eliminate the effect of the residual charge from previous electrifications. The guard electrode used in this measurement consisted of a piece of tinfoil wrapped tightly around the hard-rubber bushing as shown in figure 1. A fine wire was wrapped around the tinfoil to hold it in place and to afford a means of connecting it to the ground.

VI. RESULTS

The results were obtained under several different conditions. However, it was not thought advisable to divide the results into groups according to the different conditions which existed, since the variation between groups was no larger than that between the individual specimens of a single group. The composition of the various specimens and the conditions under which they were measured are given in table 1. The percentages of sulphur are given in the first column and the variety of rubber used is given in the second column. The third column gives the number of specimens of each which were measured. The kind of wire used as the core is given in the fourth column, and the method of vulcanization is given in the fifth column. The sixth column shows whether water or mercury was used as the pressure medium. The seventh column shows which of the specimens had the temperature controlled at 25° C during measurement, while the last column gives the gage which was used to measure the pressure.

The specimens were made from three varieties of rubber as was mentioned previously. No consistent difference between the specimens made from upriver fine Para and smoked sheet could be observed. As pointed out by Scott, McPherson, and Curtis the electrical properties of specimens made from purified rubber were slightly different from those made from unpurified rubber.[11] However, it was found that the change with pressure was about the same regardless of whether the rubber was purified or not. Because of this fact and because only four specimens made from purified rubber were measured, the results for these specimens were not grouped separately.

Two kinds of wire were used in preparing the specimens. Tinned copper wire was used in the earlier specimens, but when it was found that the tinning did not prevent action between the copper and the sulphur in the rubber, this was discarded in favor of aluminum wire. Comparison of results, however, failed to disclose any consistent difference between specimens made with the two kinds of wire.

Most of the pressure measurements were made with a pressure gage of the Bourdon tube type. This instrument was found to have errors as large as 10 percent which depended on whether the pressure had just been increased or decreased. The pressures were measured with the more accurate resistance pressure gage, described in a former paper, when this instrument became available.[12] However, measurements were made with this gage in only four cases. The measurements made with the Bourdon tube gage were corrected as best they could be but the inaccuracy of the pressure measurements is one of the sources of error in the results.

[11] BS J. Research 11, 173 (1933) RP585.
[12] J. Research NBS 14, 99 (1935) RP760.

TABLE 1.—*Composition of specimens and conditions of measurement*

Combined sulphur[a]	Rubber used	Number of specimens	Wire core	Vulcanized in—	Pressure medium	Temperature control	Pressure gage
Percent							
0	Fine Para	1	Copper		Mercury	None	Bourdon.
2	do	3	do	Steam	do	do	Do.
4	do	1	do	do	do	do	Do.
4.9	do	2	do	do	Water	do	Do.
[b]5	Smoked sheet	1	do	do	do	do	Do.
5.4	do	2	do	do	do	do	Do.
6	Fine Para	1	do	do	Mercury	do	Do.
6	Purified	1	Aluminum	CO_2	do	25° C	Resistance.
8	do	1	do	do	do	do	Do.
8	Fine Para	1	do	Hydrogen	do	None	Bourdon.
8	do	1	Copper	Steam	do	do	Do.
[b]8.5	Smoked sheet	1	do	do	Water	do	Do.
[b]10	do	2	do	do	do	do	Do.
10	Fine Para	1	do	do	Mercury	do	Do.
10	do	1	Aluminum	do	do	do	Do.
10	Purified	1	do	CO_2	do	25° C	Resistance.
[b]11.5	Smoked sheet	1	Copper	Steam	Water	None	Bourdon.
12	Purified	1	Aluminum	CO_2	Mercury	25° C	Resistance.
12	Fine Para	1	do	Hydrogen	do	None	Bourdon.
[b]13	Smoked sheet	1	Copper	Steam	Water	do	Do.
13.5	Fine Para	1	do	do	Mercury	do	Do.
13.5	do	1	Aluminum	do	do	do	Do.
[b]14.5	Smoked sheet	1	Copper	do	Water	do	Do.
16	Fine Para	1	do	do	Mercury	do	Do.
[b]16	Smoked sheet	1	do	do	Water	do	Do.
[b]17.5	do	1	do	do	do	do	Do.
18	Fine Para	2	do	do	Mercury	do	Do.
18.1	do	2	do	do	Water	do	Do.
19	do	1	do	do	Mercury	do	Do.
19	do	1	Aluminum	do	do	do	Do.
[b]19	Smoked sheet	1	Copper	do	Water	do	Do.
20	Fine Para	1	do	do	Mercury	do	Do.
22	do	1	do	do	do	do	Do.
[b]24	Smoked Sheet	1	do	do	Water	do	Do.
26	Fine Para	1	do	do	Mercury	do	Do.
32	do	1	do	do	do	do	Do.
32	Smoked sheet	2	do	do	Water	do	Do.

[a] The sulphur content was assumed to be that which was mixed into the compound in all cases, except for 4.9, 5.4, and 18.1 percent of sulphur. These specimens were analyzed for sulphur when it was discovered that sulphur migrated to the talc during vulcanization in steam. The other specimens vulcanized in steam were not then available for analysis.

[b] These specimens were not measured through a pressure cycle until after they had been under pressure for about a month.

Another source of error in the results is the lack of temperature control. Most of the measurements had been made before the importance of temperature control was realized. Only the last four specimens were measured under controlled-temperature conditions. The temperatures of the other specimens varied from 18.5 to 26.5° C. with most of the measurements being made at temperatures between 20 and 22° C.

The two pressure media, water and mercury, were used so that the possible effect of water absorption might be studied. Measurements with mercury as the pressure medium gave results for the specimen in the dry condition. With water as the pressure medium the effect of progressive water absorption could be studied.

1. DIELECTRIC CONSTANT

The effect of pressure on the dielectric constant is shown in figure 2, where the dielectric constants at atmospheric pressure (approximately 1 bar) and 700 bars are plotted as functions of the sulphur content.

These curves were obtained from measurements made on the 34 specimens immediately after they had been placed in the apparatus. The curve for 1 bar is the same as that reported in the paper by Curtis, McPherson, and Scott.[13] The irregularity of the measured values at 1 and 700 bars is about the same. At 700 bars two-thirds of the specimens yielded values which agreed with the values given by the curve within 1 percent. The difference was greater than 2 percent in only six cases. The maximum difference was 6 percent which was obtained for the specimen containing 18.1 percent of sulphur.

Increasing the pressure moved the maximum to lower percentages of sulphur and decreased the height of the maximum. This is the same effect as was obtained by decreasing the temperature as reported by Scott, McPherson, and Curtis.[14] A change of 700 bars pressure

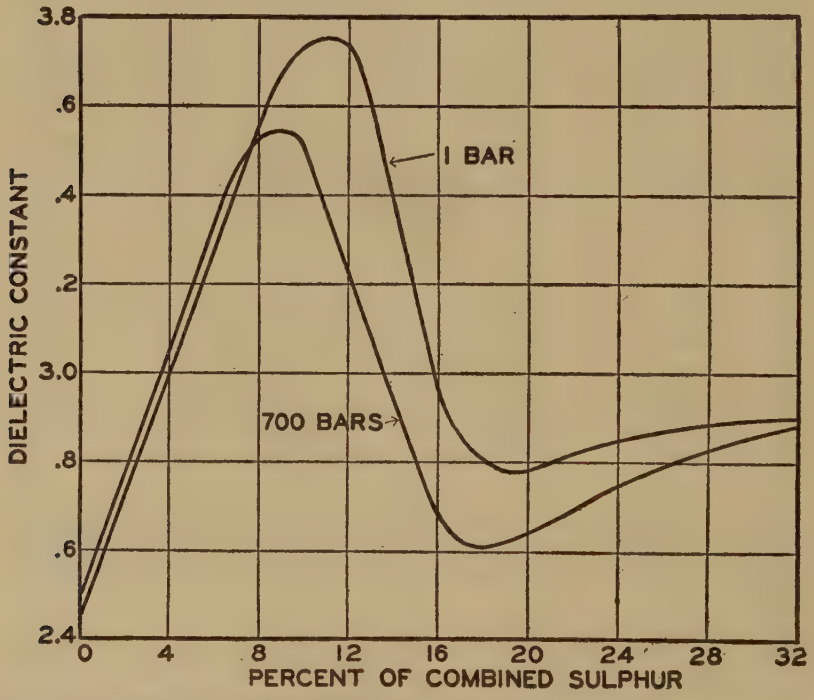

FIGURE 2.—*Change of the dielectric constant of rubber-sulphur compounds with sulphur content, at 1 and at 700 bars.*

had the same effect as a change in temperature of 12 to 20° C., the average being about 16° C. The dielectric constant for specimens containing up to about 7.5 percent of sulphur was increased slightly by pressure. For higher percentages of sulphur the dielectric constant was decreased by pressure. The maximum change with pressure occurred for about 12 percent of sulphur, while for 32 percent of sulphur the decrease with pressure was small.

The dielectric constant was, in most cases, a linear function of the pressure between 1 and 700 bars pressure. There were two ranges of

[13] BS Sci. Pap. 22, 398 (1927) S560.
[14] BS J. Research 11, 173 (1933) RP585.

sulphur content where it was not a linear function of the pressure, one range being between about 8 and 10 percent of sulphur and the other being between about 16 and 24 percent of sulphur. The results for a few representative specimens are shown in figure 3 where the dielectric constants are plotted against the pressure. Two of these, 0 and 4 percent of sulphur, were selected from the sulphur range where the dielectric constant was increased by pressure. The total increase for a pressure change of 700 bars was small, but the increase of the dielectric constant with pressure was uniform. The specimen containing 8 percent of sulphur came at about the boundary between the sulphur range where the dielectric constant increased with pressure and the

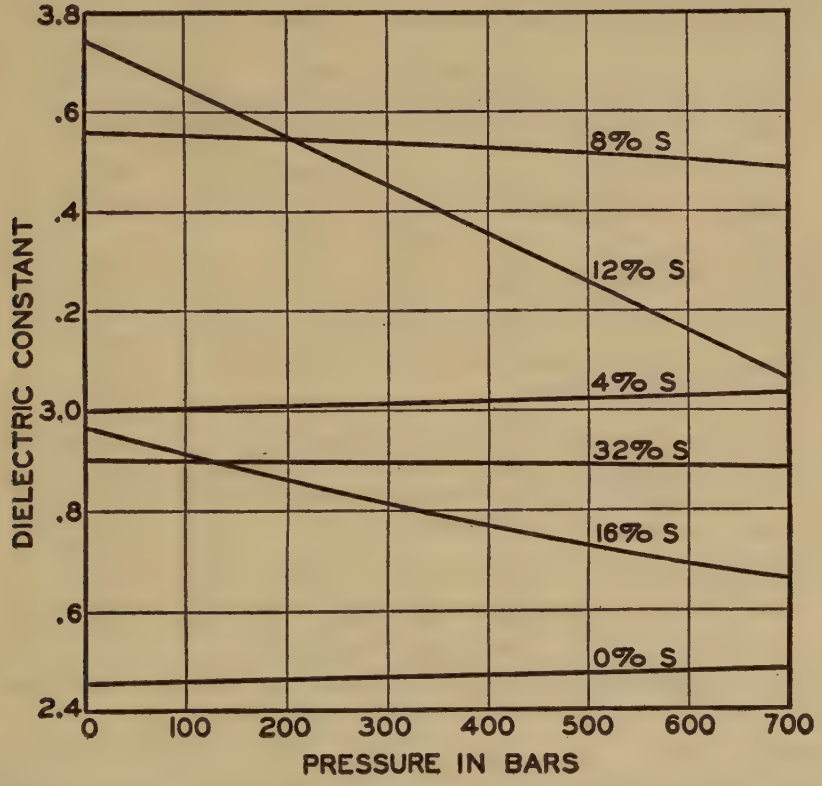

FIGURE 3.—*Change of the dielectric constant of various rubber-sulphur compounds with pressure.*

sulphur range where the dielectric constant decreased with pressure. This was also in one of the ranges where the dielectric constant was not a linear function of the pressure. The change with pressure was small for this specimen but was larger at the high pressures than at the low pressures. Three specimens, 12, 16, and 32 percent of sulphur, were selected from the sulphur range where the dielectric constant decreased with pressure. For 12 and 32 percent of sulphur, the dielectric constant was a linear function of the pressure, but for 16 percent of sulphur, the change with pressure became less as the pressure was increased.

The specimens for which water was used as the pressure medium were kept under pressure for a month or more to determine the effect which this would have on the change of the electrical properties with pressure. It was found that for the specimens containing low percentages of sulphur the electrical properties changed with time under pressure, but that for specimens containing over 18 or 20 percent of sulphur there was little change. The results for two representative specimens are shown in figures 4 and 5. Figure 4 shows the change of the dielectric constant of specimens containing 4.9 and 32 percent of sulphur with time under 655 bars pressure. The dielectric constant of the specimen containing 4.9 percent of sulphur increased rapidly with the time under pressure for the first few days, after which the change with time became much less. This curve is similar to the one published by Curtis and McPherson [15] for a flat specimen at atmospheric pressure, except that a period of days was required

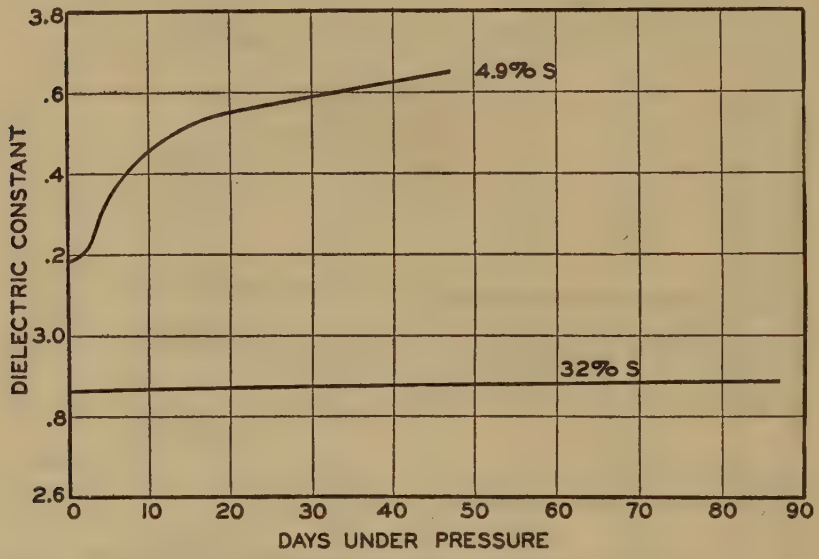

FIGURE 4.—*Change of the dielectric constant of two rubber-sulphur compounds with time under 655 bars pressure in water.*

for the dielectric constant to approach constant value while only hours were required in the case of the flat specimen. This difference in time may, in part, be accounted for by the fact that the flat specimen was thinner than the cylindrical specimen and that it was exposed to water on both sides while the cylindrical specimen had only one surface exposed to the water. The difference in composition of the specimens may have been an added factor in this difference in time. The curve in figure 4 is of the same type as that obtained by Lowry and Kohman [16] for absorption of water under pressure. The change of the dielectric constant with time under pressure, therefore, seems to be a function of the water absorption alone.

The dielectric constant of the specimen containing 32 percent of sulphur did not change materially with time under pressure. This

[15] Tech. Pap. BS **19**, 718 (1925) T299.
[16] J. Phys. Chem. **31**, 23 (1927).

was to be expected if the dielectric constant is a function of the water absorption, since hard rubber absorbs very little moisture.

Figure 5 shows the manner in which the dielectric constant of the specimen containing 4.9 percent of sulphur changed with pressure after various lengths of time under pressure in water. The curves are practically parallel, which shows that the effect of pressure is about the same regardless of the time that the specimen has been under pressure. If the only effect of continued pressure under water is the absorption of water by the rubber, then this is equivalent to saying that the effect of pressure is about the same regardless of the amount of water absorbed. The dielectric constant of the specimen containing 32 percent of sulphur changed so little with time under pressure that no curves showing the effect of pressure are given other than the one in figure 3.

A few specimens were kept under pressure in mercury for about a month. The dielectric constant increased only slightly during this time and this small change was probably not significant.

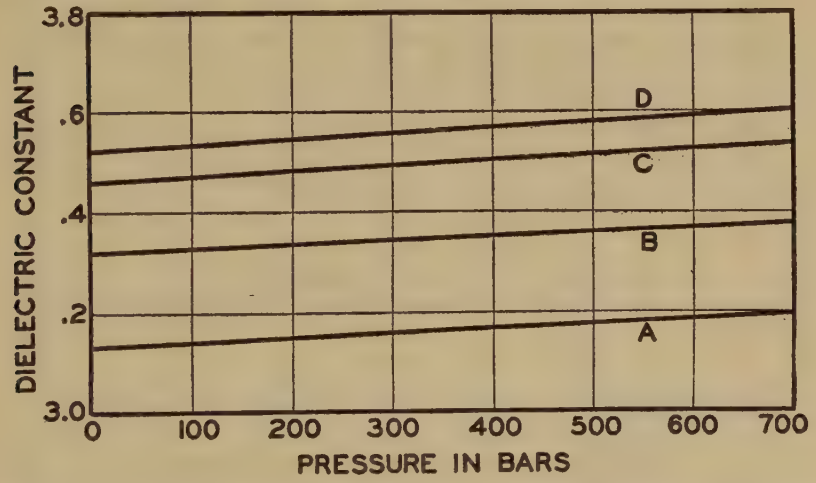

FIGURE 5.—*Change of the dielectric constant of a specimen containing 4.9 percent of sulphur with pressure after different lengths of time under 655 bars pressure.*

A, at beginning; B, after 6 days; C, after 18 days; D, after 33 days.

2. POWER FACTOR

The effect of pressure on the power factor is shown in figure 6 where the power factors at 1 and 700 bars are shown as functions of the sulphur content. These curves were drawn as average curves through the plotted points. The irregularity of the power factor values was large compared with the irregularity of the dielectric constant values. Of the 34 specimens which were measured, 10 had values of the power factor which differed from the values on the curve by more than 20 percent. Of these, 5 differed by more than 40 percent. Two of these latter specimens, 1 of which contained 6 percent of sulphur and the other 18.1 percent of sulphur, had power factors which differed from the values on the curve by about 85 percent. This irregularity was larger than was obtained for the flat specimens at atmospheric pressure.

Increasing the pressure moved the maximum to lower percentages of sulphur. The height of the maximum apparently was not changed by pressure. This was the same type of change that was observed by Scott, McPherson, and Curtis for a change in temperature.[17] The amount of the change brought about by an increase of 700 bars was about the same as was obtained for the temperature changes determined for the dielectric constant.

Although the irregularity of the measured values was large, the character of the change with pressure was consistently that represented by these curves. The power factors of all the specimens containing up to 2 percent of sulphur were very nearly independent of

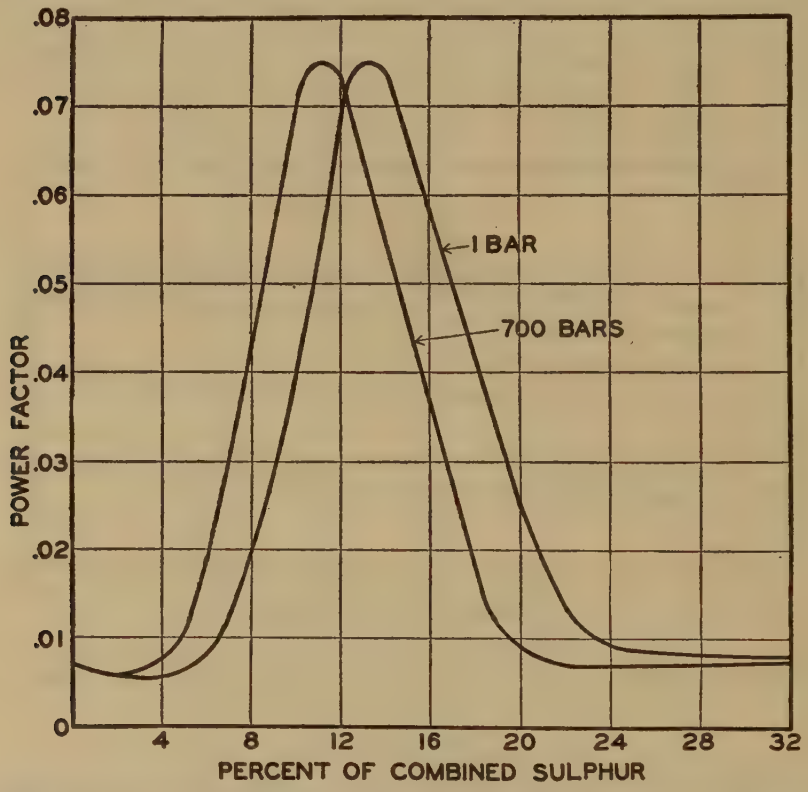

FIGURE 6.—*Change of the power factors of rubber-sulphur compounds, at 1 and at 700 bars, with sulphur content.*

pressure. The power factors at 700 bars were higher than those at 1 bar for all the specimens containing from 4 to about 12 percent of sulphur, while for percentages of sulphur higher than this, the power factors at 700 bars were lower than at 1 bar, with one exception. The values of the power factors of specimens containing 13.5 percent of sulphur increased with pressure at the low pressures and decreased with pressure at high pressures, so that the values at 700 bars were about those at 1 bar. This does not agree with figure 6.

[17] BS J. Research **11**, 173 (1933) RP585.

The power factor was a nonlinear function of the pressure in most cases for pressures between 1 and 700 bars. The manner in which the value of the power factor varied with the pressure is shown in figure 7 where the power factors for a few representative specimens are plotted against the pressure. The specimen containing no sulphur was selected from the sulphur range where the power factor was unaffected by pressure. The specimens containing 4 and 8 percent

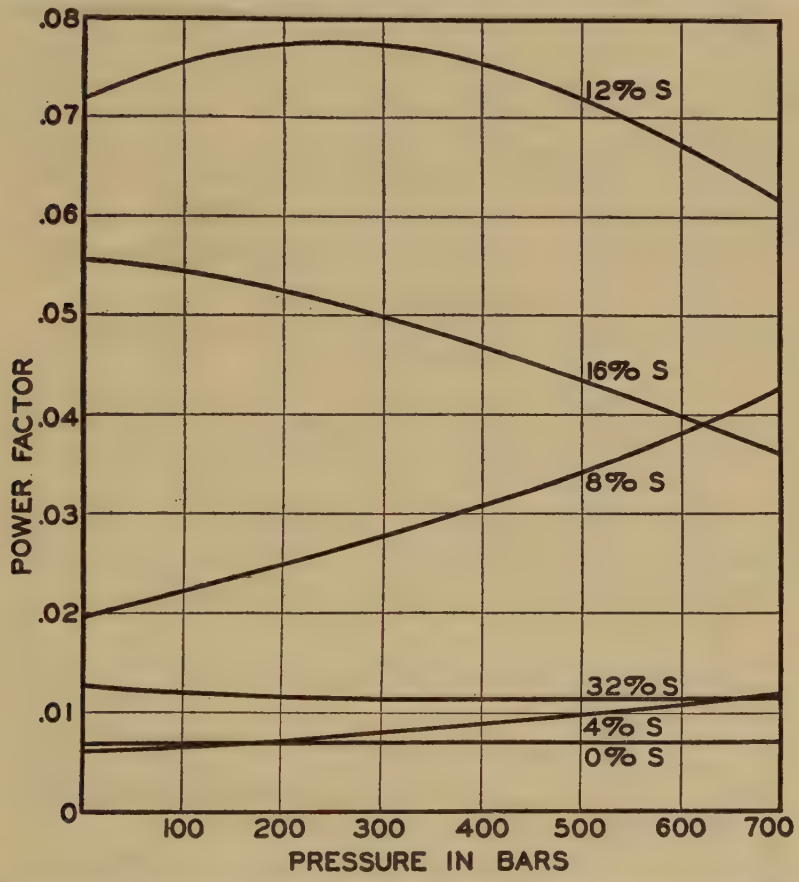

FIGURE 7.—*Change of the power factors of various rubber-sulphur specimens with pressure.*

of sulphur were selected from the range where the power factor increased with pressure. The curves for these are concave upward. The specimen containing 12 percent of sulphur was in the range where the power factor passed through a maximum with pressure. The curve for this specimen is concave downward and the maximum occurs at about 250 bars. The specimens containing 16 and 32 percent of sulphur are from the sulphur range where the power factor decreased with pressure. The curve for 16 percent of sulphur is concave downward while that for 32 percent of sulphur is concave upward. In only one other case beside those for 0 and 2 percent of sulphur was there indication that the power factor was a linear function of the pressure. The power factors of 2 of the specimens con-

taining 10 percent of sulphur were linear functions of the pressure. The power factor of the third, which was made from purified rubber, was not a linear function of the pressure and its curve was concave downward.

The change of the power factor with time under a pressure of 655 bars in water is shown for two specimens in figure 8. The power factor of the specimen containing 4.9 percent of sulphur increased

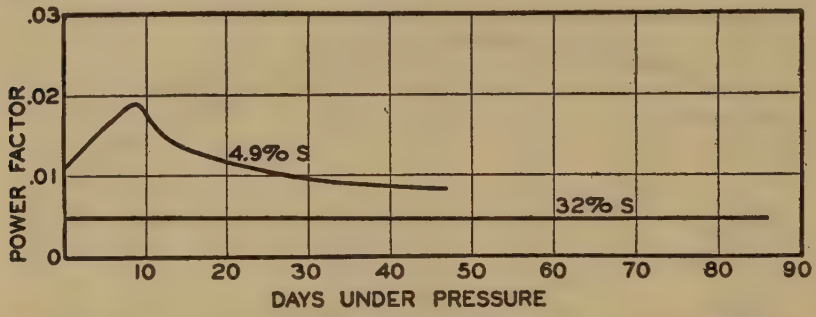

FIGURE 8.—*Change of the power factors of two rubber-sulphur specimens with time under 655 bars pressure.*

for a few days and then decreased to a value lower than that at the beginning. This curve is similar to the one published by Curtis and McPherson for a flat specimen.[18] However, the time to reach maximum was quite different in the two cases. It required only about 10 hours to reach maximum for the flat specimen, but required about 9 days for the cylindrical specimen under pressure. As explained in the case of the dielectric constant, the difference in time may be

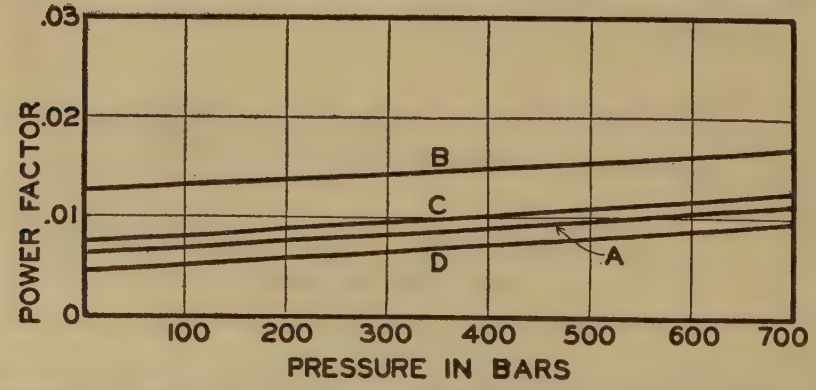

FIGURE 9.—*Change of the power factor of a rubber-sulphur specimen containing 4.9 percent of sulphur with pressure after different lengths of time under 655 bars pressure.*

A, at beginning; B, after 6 days; C, after 18 days; D, after 33 days.

due to the difference in shape and composition. The power factor of the specimen containing 32 percent of sulphur did not change appreciably with time under pressure.

The manner in which the power factor of the specimen containing 4.9 percent of sulphur changed with pressure after various periods under pressure is shown in figure 9. These curves are slightly con-

[18] Tech. Pap. BS 19, 718 (1925) T299.

cave upward but are approximately equidistant from each other at all pressures. Thus, the only effect of time under pressure was to change the values but not to change the slopes of the curves. The curves for the specimen containing 32 percent of sulphur were practically unaffected by time under pressure and so no curves are shown for it, except the one in figure 7.

3. CONDUCTIVITY

The effect of pressure on the conductivity is shown in figure 10 where the conductivities at 1 and 700 bars are shown as functions of the sulphur content. These curves show the general average of values,

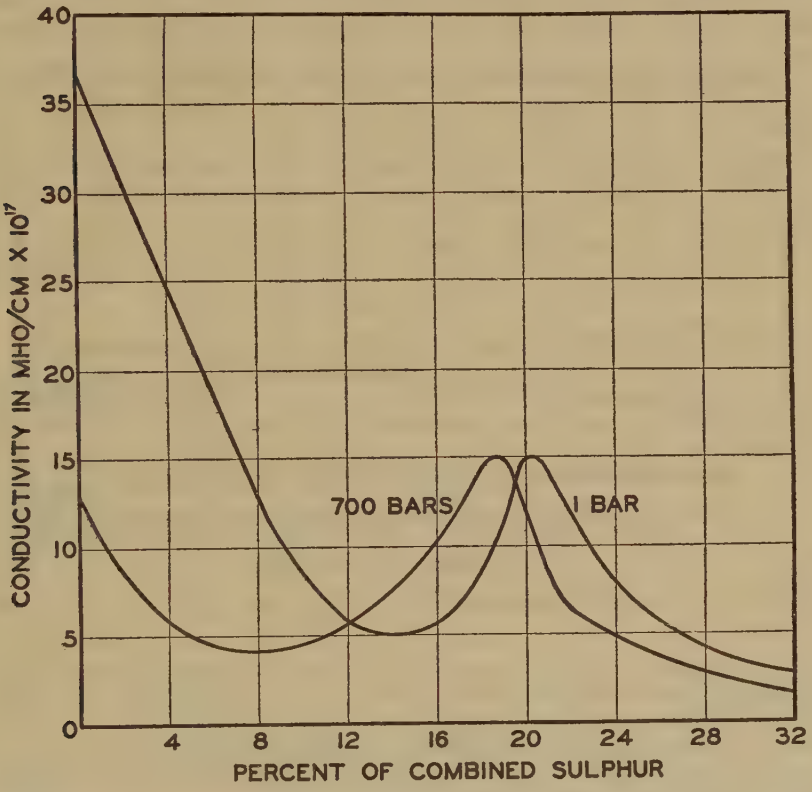

FIGURE 10.—*Change of conductivities of rubber-sulphur compounds at 1 and 700 bars with sulphur content.*

although the irregularity of the measured values was large. About half of the specimens had measured conductivities which differed at 1 or 700 bars from the curve values by more than 40 percent. Of these, 5 specimens had conductivities which differed from the curve values by more than 60 percent. In one case the difference was more than 80 percent. The conductivity of the single specimen containing no sulphur at 1 bar exceeded the value shown on the curve by about 230 percent. The value shown on the curve is in agreement with the measurements on flat specimens.

The maximum of the conductivity curve was moved to lower percentages of sulphur by increased pressure as were the maxima for dielectric constant and power factor. This change is in the same direction as was obtained by Scott, McPherson, and Curtis, for a decrease in temperature.[19] The change with pressure at low percentages of sulphur has no counterpart in the change with temperature as observed by them, since the conductivities of the specimens made from purified rubber, which they used, were about as low in the low-sulphur range as in the high-sulphur range.

Although the irregularity in results was large, the sign of the change with pressure was nearly always that indicated by the curves. The conductivity at 700 bars was lower than at 1 bar for all specimens containing up to 10 percent of sulphur and above 19 percent of sulphur. For 12 percent of sulphur, the conductivity did not change

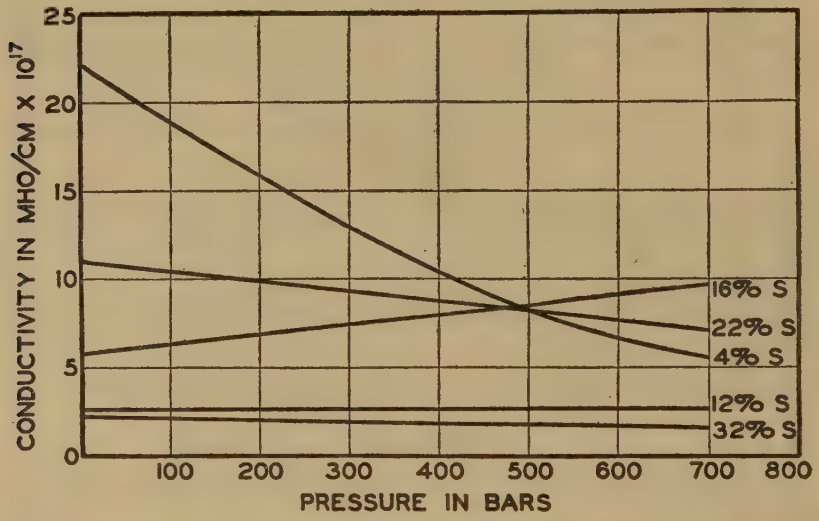

FIGURE 11.—*Change of the conductivity of various rubber-sulphur specimens with pressure.*

with pressure. For specimens containing 13.5 to about 19 percent of sulphur, the conductivity at 700 bars was higher than at 1 bar, except for the specimen containing 18.1 percent of sulphur.

The general manner in which the conductivity changed with pressure between 1 and 700 bars is shown in figure 11, where the conductivities of a number of representative specimens are plotted against the pressure. The specimen containing 4 percent of sulphur was selected from the low-sulphur range, where the conductivity decreased with pressure. The curve for this specimen is concave upward, as are the curves for all the specimens except one in this range. The curve for one of the specimens containing 2 percent of sulphur was apparently a straight line. The specimen containing 12 percent of sulphur came between the two ranges, in one of which the conductivity decreased with pressure and in the other increased with pressure.

[19] BS J. Research 11, 173 (1933) RP585.

The conductivity of this specimen was independent of pressure. The specimen containing 16 percent of sulphur was selected from the sulphur range where the conductivity increased with pressure, and the specimens containing 22 and 32 percent of sulphur were selected from the high-sulphur range where the conductivity decreased with pressure. Except in the first range, the conductivity was generally a linear function of the pressure. The few exceptions are probably not significant since duplicate specimens would have conductivities, one of which was a linear and the other a nonlinear function of the pressure.

4. DIELECTRIC CONSTANT, POWER FACTOR, AND CONDUCTIVITY OF GUTTAPERCHA

Two specimens of the guttapercha used in cable manufacture were measured under pressure in water. The results are shown in figure 12 for comparison with the results on the rubber-sulphur compounds. The dimensions were not corrected for compression of the guttapercha since it was not known. It probably would not decrease the dielectric constant at 700 bars by more than 2 percent. The correction for conductivity would be less than the experimental error. It is seen that the dielectric constant is not greatly affected by pressure. The power factor increased with pressure while the conductivity decreased with pressure.

VII. DISCUSSION OF RESULTS

This investigation has been in progress over a number of years and during that time several improvements in technique and methods of measurement were made, as described above. It was not practical to make a complete set of measurements under the improved conditions. It is therefore necessary to keep in mind the variation in conditions in studying the results.

The values of the dielectric constant were the most consistent of the electrical properties measured. As mentioned above, the measurements under pressure were made at room temperature for the most part. A study of the change of the dielectric constant with temperature led to the conclusion that the irregularities of the temperature could not explain the irregularities in the dielectric constant.

The irregularity in the power factor determinations was very large compared with that of the dielectric constant and was much larger than was obtained by Scott, McPherson, and Curtis in their work with the flat specimens at atmospheric pressure.[20] A consideration of the temperatures at which the measurements were made led to the conclusion that only a part of the irregularity in power-factor determinations could be accounted for by the diversity of temperatures.

It is possible that a part of the irregularity observed in the values of the electrical properties is due to an inaccurate assignment of composition. The amount of sulphur in the specimen was assumed to be that which was put into the mixture. Late in the investigation it was found that in some cases significant amounts of sulphur migrated from the rubber compound into the talc during vulcanization in steam. Thus, the composition of the cylindrical specimen was not the same as the flat specimen made from the same batch of mixture. Most of

[20] BS Sci. Pap. 22, 398 (1927) S560.

the specimens had deteriorated so badly that they had been discarded before it was realized that an analysis should have been made. The six specimens that were vulcanized suspended in an inert gas suffered no significant loss of sulphur during vulcanization. The assigned sulphur contents of the others may be in error by varying amounts. Even this, however, would not explain all the irregularity in the results of the power factor determinations. In two cases, supposedly

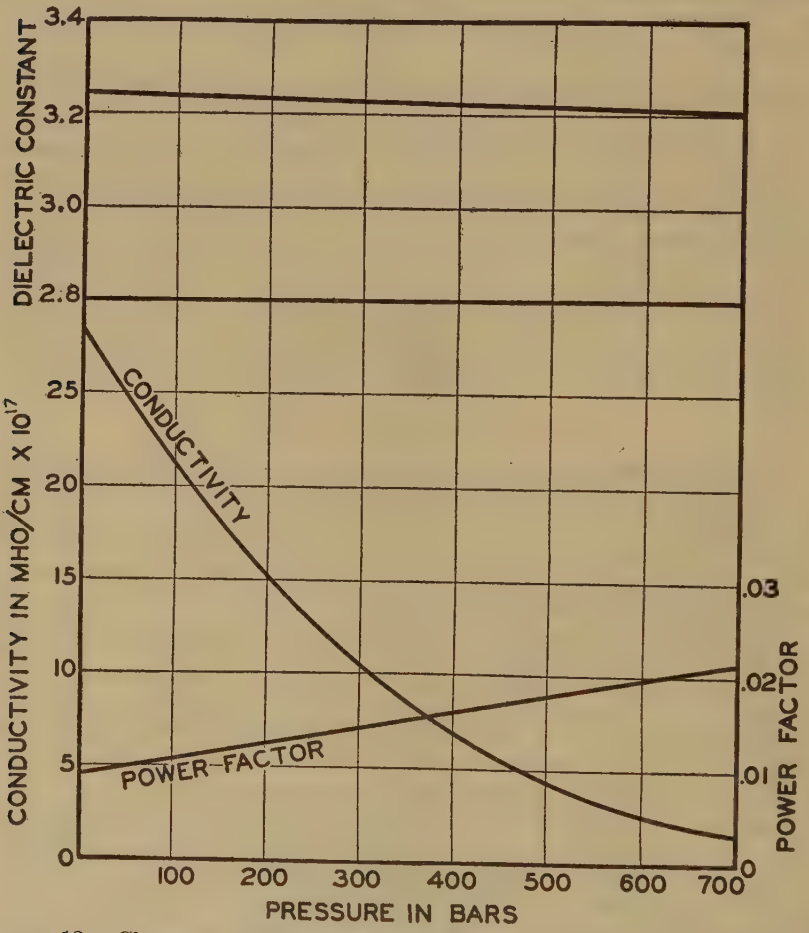

FIGURE 12.—*Change of the dielectric constant, power factor, and conductivity of guttapercha with pressure.*

identical specimens having about the same value of the power factor at 1 bar had quite different values at 700 bars.

The irregularity in the results of the conductivity determinations was no greater than might be expected from such measurements. It is significant, however, that the value of the conductivity decreased with pressure in rather definite sulphur ranges and increased with pressure in other ranges.

Only a negligible part of the power factor can be accounted for by the 1-minute conductivity. Assuming the specimen having the highest conductivity to be a perfect capacitor in parallel with a conductance equal to the 1-minute conductivity of the specimen, the computed power factor due to this conductance would be about 1×10^{-6}. This is about $\frac{1}{1000}$ of the lowest power factor which was measured.

The outstanding feature of these results is that the effect of pressure is not the same for all ranges of sulphur content. Each of the three electrical properties measured increased with pressure in certain sulphur ranges and decreased with pressure in other ranges. The changes were such that the maximum for each property was moved to lower percentages of sulphur with increased pressure. It is quite evident from this that some phenomenon other than a change in density is occurring.

These results can be qualitatively explained by the dipole or an equivalent theory as first suggested by Kitchen to explain the changes with temperature.[21] Under the dipole theory, the curves for dielectric constant in figure 2 are explained as follows: The rubber molecule is nonpolar. The addition of sulphur to the rubber molecules produces dipoles which presumably reside in the carbon-sulphur linkages and which thus increase the dielectric constant by amounts which are proportional to the combined sulphur. This explains the linear relationship between the dielectric constant and percentage of sulphur between 0 and about 9 percent of combined sulphur at the pressure of 1 bar. However, the hardness of the rubber also increases with the sulphur content. This increases the restrictive forces on the dipoles and at certain percentages of sulphur these forces seriously interfere with the motions of the dipoles so that they cannot readily follow the electric field at the frequency used in the measurement of the dielectric constant. Thus, the dielectric constant is not as large as it would be if the dipoles were able to move freely. As still more sulphur is added the rubber becomes harder, the motions of the dipoles are more restricted and the dielectric constant is thus decreased, although the number of dipoles has been increased. When sufficient sulphur has been added so that the restrictive forces on the dipoles allow only a negligible motion of the dipoles, the dielectric constant is due only to the separation of the charges in the atom and the relatively flat portion of the curve above about 19 percent of sulphur at 1 bar is obtained.

Scott, McPherson, and Curtis have shown that this curve is modified by changes in temperature.[22] The maximum is decreased and moved to a lower percentage of sulphur by a decrease in temperature. The same effect was produced by an increase of pressure as is shown in figure 2. Decreasing the temperature and increasing the pressure both make the rubber harder, which means that the restrictive forces on the dipoles have been increased. In the low-sulphur range the restrictive forces are still negligibly small for the frequency used. The dielectric constant in this range is slightly increased by a decrease of temperature or an increase of pressure because of the closer packing of the molecules. In the sulphur range where the restrictive forces are large enough to appreciably interfere with motions of the dipoles, that is, above about 8 percent of sulphur, an increase of the restrictive

[21] J. Am. Inst. Elec. Eng. 48, 281 (1929).
[22] BS J. Research 11, 173 (1933) RP585.

forces, brought about by a decrease in temperature or an increase in pressure, materially decreases the motion of the dipoles, thereby decreasing the dielectric constant.

On the basis of the dipole theory, the part of the power factor represented by the peaks in the curves in figure 6 is due to the dipoles. The energy loss in the dielectric, which is due to the dipoles, is proportional to the product of the amount of motion of the dipole and the resistance to motion which it encounters. Thus, at low percentages of sulphur, the dipole contributes a negligible amount to the power factor since the restrictive forces on the dipole are negligible and the dipole rotates freely with the electric field. The low power factor which is obtained is due to other causes. At high percentages of sulphur the dipole contributes a negligible amount to the power factor since the restrictive forces are so great that only negligible motion of the dipole is possible. Here, again, the low power factor which is obtained is due to other causes. In the intermediate-sulphur range where motion of the dipole and an appreciable resistance to its motion are both present, the power loss due to the dipole is added to the loss due to other causes and a peak is obtained in the power-factor curve.

The peak of the power-factor curve is modified by temperature in a manner similar to pressure. Scott, McPherson, and Curtis have shown that the maximum is moved to a lower percentage of sulphur by a decrease in temperature. It will be seen, from figure 6, that an increase in pressure gives the same effect. On the low-sulphur side of the peak, where the restrictive forces are so small that the dipoles are still able to approximately follow the electric field, an increase in the restrictive forces increases the power factor. On the other side of the peak, where the restrictive forces are so large that the dipoles can only partially follow the electric field, an increase in the restrictive forces materially decreases the motions of the dipoles, thereby decreasing the power factor.

The similarity of the behavior of the maximum for the conductivity to that of the power factor suggests the idea that the part of the conductivity represented by the maximum might be due to dipole motion. This would mean that for certain values of the restrictive forces the dipoles rotate so slowly under the force of the applied field that they are still yielding at the end of 1 minute. The change of the restrictive forces on the dipoles by temperature or pressure changes would move the maximum in a manner similar to that shown in figure 10. The high values of the conductivity at the low percentages of sulphur are probably due to impurities which can be eliminated by purification of the rubber, since the curve for the conductivity of specimens made from purified rubber and sulphur given by Scott, McPherson, and Curtis does not rise appreciably at the low-sulphur end.

WASHINGTON, March 13, 1935.

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VITA

ARNOLD HENRY SCOTT, son of Walter Stanley Scott and Sylvia Steele Scott, was born in Sutherland, Iowa on August 20, 1899. He received his grammar school training in a number of small towns in eastern South Dakota where his father was in the Methodist Ministry. In 1912 the family moved to Lucedale, Miss. where he finished high school. He entered the University of Mississippi in the fall of 1917. He received the degree of Bachelor of Science in 1921 and the degree of Master of Arts in 1923. In November 1925 he entered the Johns Hopkins University as a Graduate Student in the Department of Physics.

In 1919 he became laboratory Assistant in the Physics Department of the University of Mississippi and held this position for two years. The next year he was promoted to the position of Assistant Instructor and two years later he was appointed Instructor. In February, 1924 he resigned from the Staff of the University of Mississippi and became connected with the Bureau of Standards.